

The Thesis of the Doctoral (Ph. D.) dissertation

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**DETERMINATION OF RADIONUCLIDES AND
POTENTIALLY TOXIC ELEMENTS ASSOCIATED WITH
THE SPOIL BANK REMEDIATION ON THE
ENVIRONMENT AT THE ABANDONED URANIUM
MINING AREA**

By

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Title: Determination of radionuclides and potentially toxic elements associated with the spoil bank remediation on the environment at the abandoned uranium mining area

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1. Background of the work and its aims

1.1. Uranium mining in Hungary

The Mecsekérc Ltd (also known as Mecsek uranium mine was the only producer of uranium in Hungary until 1997 when it was closed due to being uneconomical ((International Atomic Energy Agency (IAEA), 2005; Malovics, 2014; Hungarian Atomic Energy Authority, 2017). In 1998 the clean-up of the uranium mining legacy started: closing of the underground mines, remediation of the rock heaps, the sedimentation ponds, and the contaminated water and of the uranium mill (Wallner and Stein, 2012). Appropriate Hungarian, as well as international laws and guidelines, IAEA recommendations, and other countries' practices, have been instrumental in setting environmental protection criteria in the remediation process (Hungarian Atomic Energy Authority, 2017). To follow the environmental protection criteria, Mecsek uranium mine conducted a long-term land reclamation which included the monitoring of air, groundwater and surface waters, soil, rocks, and vegetation as endangered and contaminated compartments in the period of mine closure, remediation, and post-closure operation (Mecsekérc Zrt., 2017). Mecsekérc Zrt (2017) further stated that it is imperative that the performance of the radon barrier is enough and that the migration of radionuclides is constantly monitored. Due to the presence of numerous elements and radionuclides, mine tailings cause severe pollution problems and may pose risks to humans (Skipperud *et al.*, 2013; Fernández-Ondoño *et al.*, 2017). Spoil deposits are high in these elements and can often be prone to water and/or wind erosion, spreading the contamination to surrounding areas. The question of environmental contamination occurs when potentially toxic elements (PTEs) and radionuclides are mobilized from the deposits of uranium-containing waste (waste rock pile, tailings ponds, etc.) into the soil and absorbed by plants or transferred to groundwater (Waggitt, 2008; Shiva Kumar and Srikantaswamy, 2014).

This study is part of the Mecsek uranium mine ongoing environmental monitoring program to monitor the endangered and contaminated compartments in the period of mine closure, remediation, and post-closure operation (Mecsekérc Zrt., 2017). Every three to five years, samples are taken from all spoil deposits and from covering soil to monitor the migration of radionuclides and potentially toxic elements (PTEs). In this monitoring program, the gamma dose rate and radon-222 (Rn-222) are measured in nGy/h and Bq/m³, respectively, and the total concentrations of elements are measured in the soil, water, and plants. Based on the results of the monitoring program, spoil deposit No. I was deemed to require further investigation on the mobility of radionuclides and PTEs. However, it is now generally understood that the distribution, mobility, and bioavailability of PTEs and radionuclides in the environment depends not only on their total concentration but also on the form of association in the solid phase they are bound to (Filgueiras *et al.*, 2002). Sequential extraction is an essential and commonly used method for obtaining knowledge about possible mobility (such as potential bioavailability and toxicity) of PTEs and radionuclides (Rauret *et al.*, 1999; Filgueiras *et al.*, 2002; Sheppard, 2011; Iurian *et al.*, 2015; Mittermüller *et al.*, 2016; Bacon and Davidson, 2017; Rosado *et al.*, 2016; Fernández-Ondoño *et al.*, 2017; Heltai *et al.*, 2018; Pérez-Moreno *et al.*, 2018). Sequential extraction procedures have not been previously included in the monitoring program for the migration of PTEs and radionuclides in the Mecsek uranium mine. Therefore, to investigate a long-term environmental impact, this research study focused on estimating the migration of these elements using the sequential extraction procedure recommended by the Community Bureau of Reference (BCR) procedure (Rauret *et al.*, 1999; Rauret *et al.*, 2001).

1.2. Aim and objectives of the study

This research aimed to study the effectiveness of the soil covering layer in retardation of the migration of PTEs and radioactive substances on the covering soil of spoil deposit No. I in Mecsek uranium mine. The goal is to use the same

methodologies used in this research study to address similar problems in South Africa. Specific objectives were:

1. To determine the total concentration levels of PTEs and radionuclides in soil, plant, and water samples collected from spoil deposit No. I and to determine if these concentrations are within the regulatory limits. Elaboration of the sampling plan based on the detected anomaly during the previous gamma activity monitoring results according to the topography of spoil deposit No. I.
2. To evaluate the mobility of PTEs and uranium in covering soil by adopting BCR sequential extraction methodology to the specific Mecsek mine conditions. To study the influence of covering soil characteristics (pH, cation exchange capacity (CEC), soil organic matter (SOM)) on mobility.
3. To study the bioavailability and uptake of PTEs and radionuclides by plants in the spoil deposit No. I using the pseudo total methodology.
4. To evaluate the efficacy of the soil covering layer retarding the migration of the PTEs, radon-222, and radionuclides in the remediated spoil deposit No. I.

2. Materials and methods

2.1. Study area

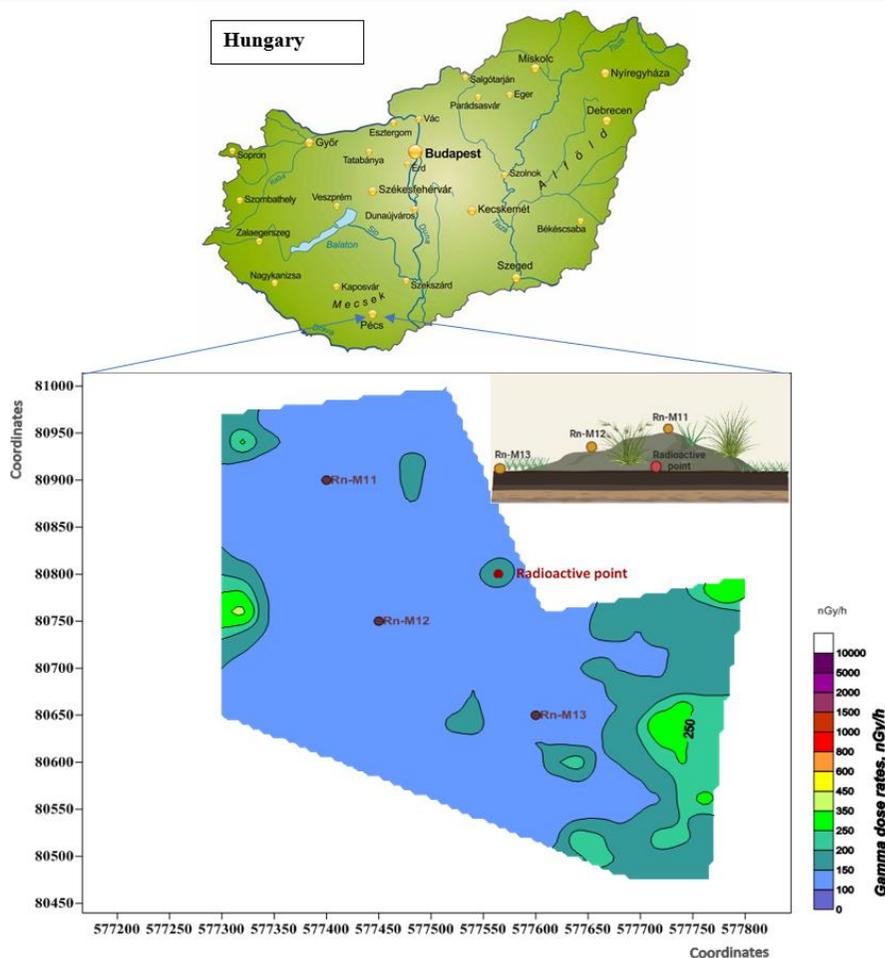


Figure 1. Site location map of Hungary (OrangeSmile.com, n.d.) and the soil and plants sampling points in Mecsek uranium mine from spoil bank No. I, Pécs, 2017 showing the gamma dose rates distribution with an insert of a schematic diagram of spoil deposit No. I

Soil and covering plant samples were collected on the 11th of July 2018 from four sampling locations in Mecsek uranium mine deposit No. I in Pécs, South-west of Hungary (Figure 1.): (1) at the top of the deposit - Rn-M11, (2) on the slope of the deposit – Rn-M12, (3) at the bottom field – Rn-M13 and (4) at the bottom edge of the slope of the deposit - radioactive point (Figure 1.) illustrates deposit

No. I with gamma dose rates that were measured previously as part of the monitoring program. Eleven water samples were collected between the 20th of October 2020 and the 27th of October 2020 during one of the routine monitoring processes conducted by the Mecsek uranium mine.

2.2. Soil, plant, and water sampling

2.2.1. Soil sampling

Core soil samples were collected using a hand auger instrument labeled with different measurements. Each soil core sample was taken from different depths: 0 – 25 cm, 25 – 50 cm, 50 – 75 cm, and 75 – 100 cm. For sample location Rn-M11, 75 – 100 cm depth could not be sampled as this was hard rock. Radioactive soil was possible to sampling only from the top 0-25 cm layer.

2.2.2. Plant sampling

Covering plant samples (a mixture of Asteraceae and Quackgrass - *Elytrigia repens*) were collected by cutting from the surface of the plants with a knife. Plant samples were collected from a 1.5 m² area of the same locations where the soil samples were also collected from (Rn-M11, Rn-M12, Rn-M13, and radioactive point) to determine if there is any biological uptake of PTEs and radioactivity from the soil.

2.2.3. Water sampling

A total of eleven water samples were collected from various places around the Mecsek mine. From these samples, six samples were groundwater samples, of which four samples (1) Pk-29/1, (2) Pk- 33/1, (3) Pk-44/3, and (4) 1504/1 were collected from monitoring well near the spoil deposit No. I and two samples (5) P-2/5 and (6) P-2/6 were collected from the water pumping well at former percolation area No. II.). One sample: (7) Északi-táró was mixed water: mine water from the spoil deposit No. III and leaking water from precipitation collected from the gravitational effluent mine water (north mines). Two samples were

seepage water (one sample: (8) CS-0 collected from the spoil deposit No. II and another sample: (9) IIIm. Gyűjtő collected from spoil deposit No. III. One sample: (10) 6/11. szint was mine water from the mine No. I collected from water pumping well. The last sample (11) Elfolyó was treated mine water collected from the mining water treatment plant. The samples were labeled based on the mine description.

2.3. Characteristics that may affect elemental mobility

Characteristics that may affect the mobility of elements were measured to determine their content in soil and plants. These characteristics include:

- ❖ Meteorological data - the average precipitation at Pécs was obtained from the meteorological data extracted from the Hungarian Central Statistical Office Websites (https1://www.ksh.hu/docs/eng/xstadat/xstadat_annual/i_met002cc.html) and (https2://www.ksh.hu/docs/eng/xstadat/xstadat_infra/e_met006.html).
- ❖ The soil and plant moisture - the amount of water present in the soil (% soil moisture) (Nielsen, 2019) and plants (% plant moisture) (Ismail, 2017) was determined.
- ❖ The soil pH - the soil pH was determined in 1 mol/l KCl (1:2.5 soil to KCl ratio) with the aid of a Glass-electrode pH meter (van Reeuwijk, 2002).
- ❖ The cation exchange capacity (CEC)- the CEC in soil was determined according to the Hungarian Standard MSZ 1484-3:2006 (2006).
- ❖ The soil organic matter (SOM) – the SOM was determined from the total inorganic carbon (percent calcium carbonate) (Bernard *et al.*, n.d.).

2.4. Radioanalytical procedure

2.4.1. Soil and plant sample preparation

Before the soil homogenizing process, Rn-222 was measured for all soil samples. After which, all soil samples were air-dried for five days. After five days, the samples were physically homogenized and grinded using Retch SM 100 with a

0.25 mm sieve instrument. Approximately 30 g of homogeneous soil samples were weighed and airtight sealed in plastic containers for the gamma-ray measurements. Samples were kept in storage for six weeks before gamma-ray analysis took place; this incubation period allows Ra-226 and its short-lived progenies to achieve secular equilibrium noting the exact dates and times from sealing was recorded.

Only the radioactive plant sample was separated into two portions, half of the sample was not washed, and the other half was washed first with low to medium pressure water for five minutes to simulate the rain. This washing process was conducted on this sample to determine whether the radioactivity concentration is due to the contamination through air particles/dust or biological uptake through the soil. After this process, all plant samples were air-dried for five days and grinded into a powder form. The grinded plant samples were weighed and airtight kept for six weeks to allow the growth of Ra-226 and its short-lived progenies before gamma-ray measurements.

2.4.2. Radon measurement by AlphaGUARD

Radon (Rn-222) was measured for each soil sample for 24 hours using Genitron Instruments AlphaGUARD PQ2000/MC50 Multiparameter Radon Monitor before the samples were counted for 24 hours each. The results were recorded every hour. The average results were recorded for each sample. The background was counted and recorded as 40.00 ± 7.00 Bq/m³. The background was then subtracted from each sample to give the final results reported in this study.

2.4.3. Gamma spectroscopy

Both homogenous soil and plant samples were measured for 3600 seconds each using CANBERRA HPGE high purity semiconductor gamma detector. The soil and plant samples were kept in storage for six weeks to attain the radioactive equilibrium between Ra-226 and the decay products with short half-lives (Júnior *et al.*, 2006). All samples have had enough time to establish secular equilibrium

between decay series products, so determining the activity of parent isotopes was possible by measuring daughter isotopes having significant gamma lines. Measured radionuclides were compared to identify the radionuclides that had the highest activity and to identify the trends of all the radionuclides as the depths of soil samples change. The activity concentrations for each soil sample were compared with the plant sample collected at the same sampling point to identify if there is any biological uptake of radionuclides. The highest contribution to this radioactivity is due to the great number of decay products of U-238 and Th-232 (Júnior *et al.*, 2006). These primordial radionuclides were measured, and the activity concentration for each was determined per depth of the soil sample and plant samples.

2.5. Pseudo total element analysis

2.5.1. Microwave digestion

Soil and plant samples were digested with microwave supported method. The microwave digestion method was conducted according to the Hungarian Standard MSZ 21470-50:2006 (2006), using CEM Mars 5 Xtraction 230/60 Microwave Accelerated Reaction System 907501, applying operational parameters proposed by the producer. After digestion, each sample was filtered into a 25 mL volumetric flask.

2.5.2. Water sample preparation

Water samples were prepared using the Hungarian Standard MSZ 1484-3:2006 (2006). Water samples were filtered into a 40 mL centrifuge tube using Munktell filter discs grade 389. The samples were measured first before adding anything to determine if they will need dilution.

2.5.3. Pseudo total elemental analysis

The total elemental content (Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, and Zn) of digested solutions was determined by a HORIBA Jobin Yvon ACTIVA M Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-

OES) using matrix-matched calibration and Yttrium internal standard with optimized operation parameters as described in Heltai *et al.* (2019).

2.6. The soil/plant transfer factor determination

The soil/plant TFs for radionuclides and PTEs were calculated to determine the possibility of these elements being taken up from the soil by the plants. The TF was calculated only from the total concentrations obtained from the 0 – 25 depth of soil sample because the grassroots are mainly in this soil depth.

2.7. BCR sequential extraction procedure

The Certified Reference Material (CRM) BCR[®]-701 for Cd, Cr, Cu, Ni, Pb, and Zn was prepared in parallel with the samples to control the accuracy of the analysis. From the extracts prepared by the procedure in (Table 1.) as described in detail by Rauret *et al.* (1999), Rauret *et al.* (2001), and Heltai *et al.* (2019). The extractable contents of the extracts (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, U, and Zn) were also determined from the 0 – 25 cm soil depth of each sample with optimized, flexible multi-elemental ICP-OES method as described by Heltai *et al.* (2019).

Table 1. The BCR sequential extraction procedure

Extraction step	Extractant reagents	Element fraction
Fraction 1	0.11 M acetic acid	Exchangeable and Acid-soluble fraction
Fraction 2	0.5 M NH ₂ -OH·HCl (adjusted to pH=1.5 by adding 25 mL 2 M HNO ₃)	Reducible species (e.g., Fe and Mn oxides, oxyhydroxides)
Fraction 3	preliminary oxidation by 8.8 M H ₂ O ₂ , then 1M NH ₄ OAc (pH=2)	Oxidizable - forms bound to organic matter or sulphides
Fraction 4	HNO ₃ /H ₂ O ₂ (microwave supported acid digestion)	Residual fraction, non-silicate bound metals

Quality control: The quality control for this study was conducted using the Certified Reference Material (CRM). This CRM BCR[®]-701 is certified for only

six elements (Cd, Cr, Cu, Ni, Pb, and Zn). The percentage recovery for each element was calculated. In order to validate the BCR sequential procedure, the sums of the cumulated concentrations for each element in Step 1 (F1) + Step 2 (F2) + Step 3 (F3) + Aqua regia step (F4) were compared to the pseudo total concentrations obtained from the same samples (0 – 25 cm depth) and given in mg/kg units.

2.8. Statistical analysis

The statistical analysis was conducted using SPSS Statistics 28 for basic descriptive statistical analysis, a one-sample t-test to determine the differences between the means of one variable, and the linear regression analysis for the determination of the soils' effect on the plants.

The principal component analysis (PCA) biplot was utilized using Analyse-it for Microsoft excel 2010 version 5.80.2 software to examine the relationships among the radionuclides, PTEs, and soil characteristics in a multidimensional dataset. The Analyse-it software was also used to plot the correlation figures and linear regression figures. To determine the common characteristics between PTEs, radionuclides, and physicochemical properties in the soil and plant samples, Pearson's correlation coefficient (r) was determined.

3. RESULTS AND DISCUSSION

3.1. Characteristics that may affect the mobility of elements

3.1.1. Meteorological conditions

The meteorological data were retrieved from the data published on the Website (https://www.ksh.hu/docs/eng/xstadat/xstadat_annual/i_met002cc.html) of the Hungarian Central Statistical Office. During the remediation period, from the time when the mine closed to a sampling of soil (1997 – 2018), the average precipitation was 674 mm with a minimum of 405 mm in 2011 and a maximum

of 981 mm in 2014. During the sampling month of July 2018, the precipitation intensity was 58 mm over thirteen precipitation days as indicated on the Website (https://www.ksh.hu/docs/eng/xstadat/xstadat_infra/e_met006.html) (Hungarian Central Statistical Office, n.d.).

3.1.2. Physicochemical characteristics

The soil physicochemical characteristics were eventually evaluated for their possible effects on plant uptake of elements and radionuclides from the soil. The soil moisture content (% SM), the average soil organic matter (% SOM), pH, CEC, and plant moisture content are indicated in (Table 2.).

Table 2. Properties that may affect the mobility of elements

Sample description	Depth (cm)	Soil moisture content (%)	Average Soil pH	CEC (cmol(+)/kg)	SOM (%)	Plant moisture content (%)
Rn-M11	0 – 25	9.24	6.22	52.9 ± 6.71	1.61	33.1
	25 – 50	7.44	6.12	20.2 ± 0.06	1.21	
	50 – 75	12.6	5.99	14.6 ± 4.55	2.56	
	75 – 100	Hard rock (not sampled)				
Rn-M12	0 – 25	9.47	5.79	33.0 ± 0.69	0.75	31.2
	25 – 50	8.99	5.50	8.23 ± 1.09	0.64	
	50 – 75	8.19	5.47	24.4 ± 1.31	0.96	
	75 – 100	8.43	5.38	33.0 ± 0.01	1.11	
Rn-M13	0 – 25	17.1	5.61	28.2 ± 0.44	5.27	25.0
	25 – 50	14.3	5.27	31.8 ± 4.61	3.34	
	50 – 75	14.2	5.38	28.1 ± 2.67	1.92	
	75 – 100	14.2	5.36	36.6 ± 0.01	1.76	
Radioactive sample	0 - 25	3.16	5.27	27.3 ± 0.01	1.31	60.3

According to the artificial forming of the cover layer, the soil parameters did not show any trend in the function of layer deepness. Along the slope position, the

pH values indicated a narrow range 5.27 - 6.22 and showed decreasing tendency from top to bottom direction. The CEC values did not follow any trend. The CEC values ranged from 8.23 ± 1.09 (cmol(+)/kg) to 52.89 ± 6.71 (cmol(+)/kg). The SOM values ranged between 0.87 % and 3.87 %.

3.2. Radioanalytical results

There have not been known limits placed for natural radionuclides (K-40, U-238, U-235, and Th-232) in the soil since K-40, Th-232, and U-238 primordial radionuclides that have existed since the beginning of Earth. However, UNSCEAR (2000) placed international median values for each radionuclide in soil and the mean values for each country based on previously reported activity concentrations in the World. Therefore, the activity concentration obtained in this study were compared to the mean concentrations for Hungary. For Rn-222, it is the obligation for each country to place a limit not to be exceeded following the regulations of the International Commission on Radiological Protection (ICRP), IAEA, and/or UNSCEAR based on the safety of the people. Hence, Hungary set the Rn-222 action level value of 1000 Bq/m^3 , which is documented in the Hungarian Regulation 10 16/2000 (2000) (Shahrokhi *et al.*, 2017). The Rn-222 activity concentrations obtained in this study were compared to the Hungarian Regulation 10 16/2000 action level value, radiation protection requirement for radon reported by the Republic of Hungary, and the activity concentrations of natural radionuclides in soil samples were compared to the international values reported by UNSCEAR (2000).

3.2.1. Radon activity concentrations

The summary of the results for Rn-222 activity concentration measurements in the soil samples is indicated in (Table 3.).

Table 3. Rn-222 activity concentration in soil

Sample name	Sample depth (cm)	Activity (Bq/m ³)
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Rn-M11	0 – 25	5.08 ± 1.34
	25 – 50	25.6 ± 1.81
	50 – 75	< background
	75 – 100	Hard rock (not sampled)
Rn-M12	0 – 25	29.3 ± 1.35
	25 – 50	29.1 ± 1.79
	50 – 75	14.3 ± 1.95
	75-100	23.0 ± 0.77
Rn-M13	0 – 25	13.5 ± 2.33
	25 – 50	49.3 ± 2.27
	50 – 75	40.2 ± 2.16
	75 – 100	44.3 ± 2.16
Radioactive sample	0 – 25	80.3 ± 1.34

The Rn-222 activity concentrations for the soil depths of Rn-M11, Rn-M12, and Rn-M13 samples were did not show a trend in depths. However, the topographic details imply that the activity concentration for Rn-222 decreases as the spoil deposit slope increases. Statistically, the sample depths and the Rn-222 concentrations indicated a weak negative correlation ($r = - 0.100$; $p = > 0.05$). The one-sample t-test results showed a significant difference ($p > 0.05$) between the sample locations, whereas only the Rn-M11 sample indicated significant differences in terms of depths.

All Rn-222 activity concentrations were below the action level value of 1000 Bq/m³ set by the Republic of Hungary (2008) for radiation protection and stated in the Hungarian Regulation 10 16/2000 (2000) for workplaces mines, tourists caves, and other underground activities.

3.2.2. Gamma spectroscopy

The soil activity concentrations for natural radionuclides measured were compared to the Hungarian mean value for the natural radionuclide content in the soil as specified by UNSCEAR (2000). When comparing the activity concentrations for all measured radionuclides, the activity concentration for K-40 was observed to be too high for the clear visual presentation of other radionuclides with low activity. Therefore, the activity concentrations for K-40 are presented separately as shown in (Figure 2.).

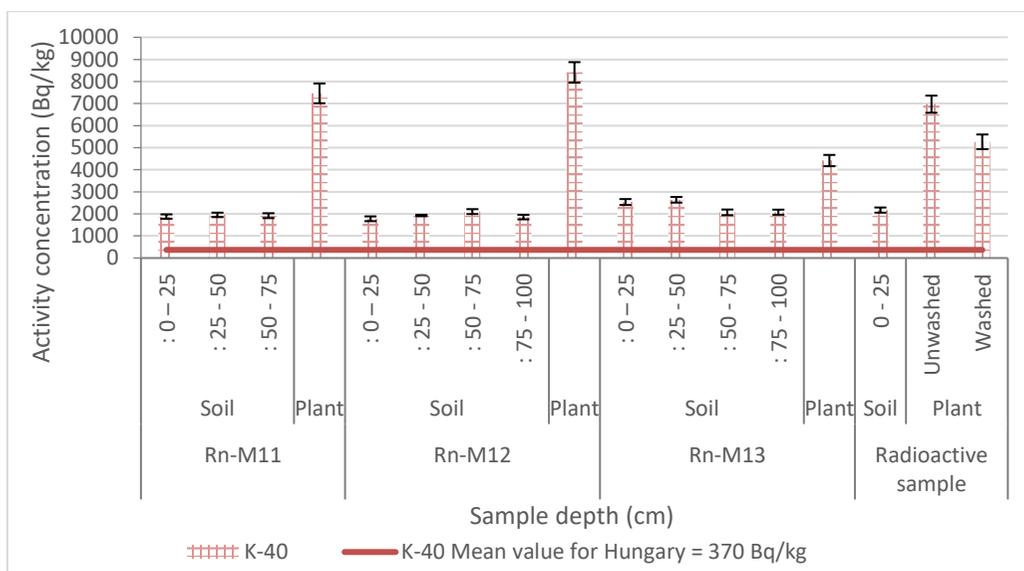


Figure 2. Activity concentrations for K-40 measured in soil and plant samples

The vertical analysis for K-40 results indicated that the soil depth did not have an impact on the concentration since similar concentrations could be obtained for each sample. The activity concentrations of K-40 in soil were all above the World's median value of 400 Bq/kg for K-40, and the concentrations were outside the range of 140 – 850 Bq/kg as reported by the UNSCEAR (2000). One-sample t-test statistical results indicated that there were no significant differences ($p \leq 0.05$) in K-40 concentrations in terms of depths and in terms of topography.

The activity concentration of K-40 in the unwashed plant samples was slightly higher than in the washed sample. This observation concludes that some of the activity concentration in plants is due to dust particles. The comparison of the results for soil samples with plant samples collected at the same location indicated that K-40 radioactivity concentrations of plant samples were more than double the soil activity concentrations. This implies that the plant samples might have taken up a large amount of K-40 from the soil.

The activity concentrations for U-238, Th-232, and U-235 radionuclides in the soil samples in each depth, and the concentrations for the plant samples collected at the same location are shown in (Figure 3.). The results for the Radioactive sample are presented separately in (Figure 4.) to show the progenies for U-238 behavior since U-238 was elevated in this location.

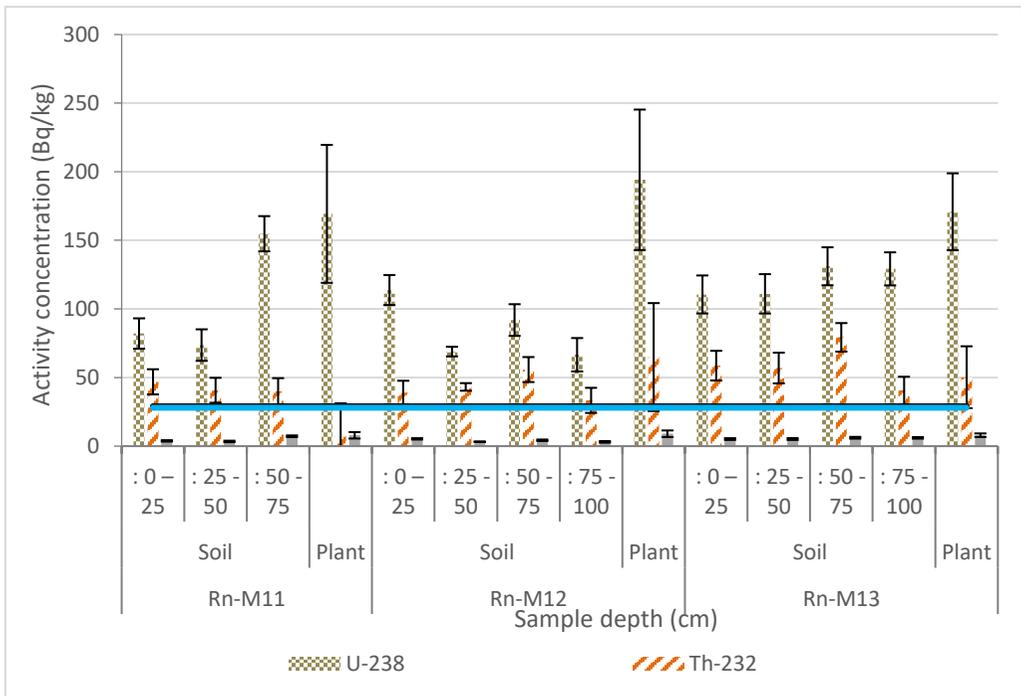


Figure 3. Activity concentrations for the natural radionuclides in soil and plant samples

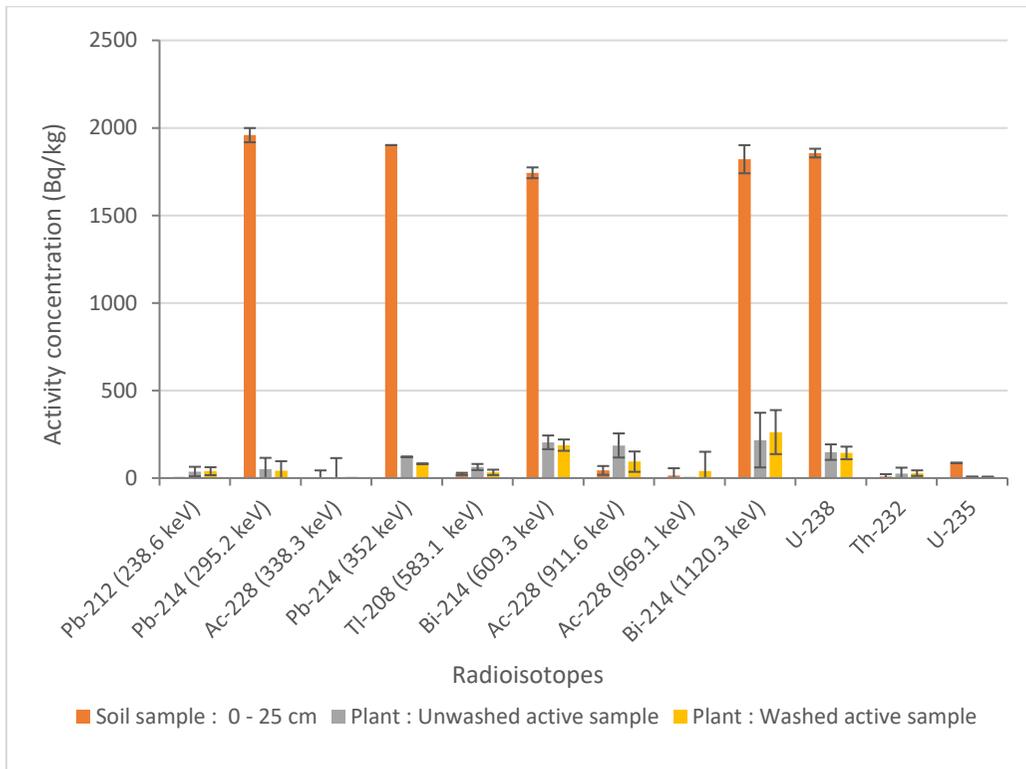


Figure 4. Radioactive sample – activity concentrations for radioactive soil and plant sample before and after washing

The results for natural radionuclides in (Figure 3. and Figure 4.) indicated that the depth of the soil did not impact the activity concentrations; there was a variation in activity concentrations. However, the topography of the deposit may have influenced the concentration results. The activity concentrations of U-238 and Th-232 in soil were all above the mean values for soils in Hungary and the median value for soils in the World as reported by UNSCEAR (2000). (UNSCEAR, 2000). Statistical results indicated that there was no significant difference in terms of the topography when considering Rn-M11, Rn-M12, and Rn-M13 ($p \leq 0.05$). In contrast, when considering the Radioactive sample, U-235 and U-238 were significantly different. In terms of depth, only Rn-M11 indicated some differences in U-235 and U-238.

The activity concentrations for all the natural radionuclides detected in plant samples were above the concentrations found in soil samples collected from the same location, with an exception for Th-232. Thorium-232 displayed an average concentration that was less than the average concentration of the soil.

Transfer factor values were determined on a mass basis as indicated in (Table 4.); the activity concentration of plant samples (dry matter) was related to the radionuclide activity concentration in the first 25 cm of soil. The TF values obtained in this study were compared to the mean values for radionuclide TF ratios (grasses) in a temperate environment for all types of soil reported by the International Atomic Energy Agency on their Technical Reports Series no. 472 (IAEA, 2011).

Table 4. Transfer Factors for radionuclides calculated from 0 – 25 cm soil samples

Radionuclides (energy line)	Rn-M11	Rn-M12	Rn-M13	Radioactive sample
Pb-212 (238.6 keV)	n.d.	1.25 ± 4.53	n.d.	n.d.
Pb-214 (295.2 keV)	1.97 ± 4.86	3.27 ± 4.45	1.16 ± 1.97	0.03 ± 1.59
Ac-228 (338.3 keV)	n.d.	1.56 ± 4.68	2.35 ± 2.05	2.44 ± 2.62
Pb-214 (352 keV)	0.16 ± 4.40	2.57 ± 4.40	0.88 ± 1.99	0.06 ± 1.24
Tl-208 (583.1 keV)	1.34 ± 4.75	6.40 ± 4.26	0.22 ± 2.18	2.64 ± 2.81
Bi-214 (609.3 keV)	3.17 ± 4.42	1.72 ± 4.53	1.11 ± 2.03	0.12 ± 1.26
Ac-228 (911.6 keV)	7.95 ± 4.37	1.68 ± 4.19	0.68 ± 2.37	4.26 ± 2.73
Ac-228 (969.1 keV)	n.d.	n.d	n.d	n.d
Bi-214 (1120.3 keV)	2.30 ± 4.51	0.85 ± 4.74	2.44 ± 2.03	0.12 ± 1.95
K-40 (1460.8 keV)	3.97 ± 4.45	4.73 ± 4.31	1.74 ± 1.91	3.21 ± 3.32
U-238	2.06 ± 4.54	1.71 ± 4.67	1.55 ± 2.02	0.08 ± 1.78
Th-232	0.16 ± 2.59	1.67 ± 4.53	0.86 ± 2.08	2.60 ± 2.71
U-235	2.06 ± 4.54	1.71 ± 4.67	1.55 ± 2.02	0.08 ± 1.78
TF values for grasses (IAEA, 2010)				
	Mean	Minimum	Maximum	
Pb	0.31	0.11	1.0	

K (in pasture grasses)	0.73	-	-
U	0.017	0.00020	5.5
Th	0.042	0.00074	0.65

The n.d. abbreviation represents not detectable.

The Pb TF ratios for the radioactive sample were all below the minimum values reported by the IAEA. In comparison, the rest of the samples contained Pb radioisotopes that were above the maximum value. The TF ratios for U-238 and U-235 were the same for all samples, which were all above the mean values but were below the maximum value of 5.5, as reported by IAEA. Only the TF ratio for Th-232 from the Rn-M11 sample was below the maximum range of the IAEA TF value for Th of 0.65. The TF ratios for K-40 were observed to be higher than the TF ratios for all the natural radionuclides. Transfer factor results indicated that there is a possibility of radionuclide uptake by plants.

3.3. Potentially toxic elements

The results for total trace elements are discussed in detail in Khumalo *et al.* (2020).

3.3.1. Pseudo total elements results

The PTE concentrations obtained by the pseudo total analysis were compared to the soil permissible limits regulated by the Hungarian Government (6/2009. IV. 14. 2009) based on the regulation of other European (EU) member countries (Rékási and Filep, 2012).

The results were presented according to the elemental importance in soil. The elements that are required by plants in large quantities (Ca, K, Mg, Fe, and P) are shown in (Figure 5.). The elements that are needed by plants in small amounts are shown in two figures for clear visibility: Co, Mn, and Cu are shown in (Figure 6.) and Na, Zn, and Ni in (Figure 7.). Lastly, the toxic elements (Cd, Cr, and Pb) are shown in (Figure 8.).

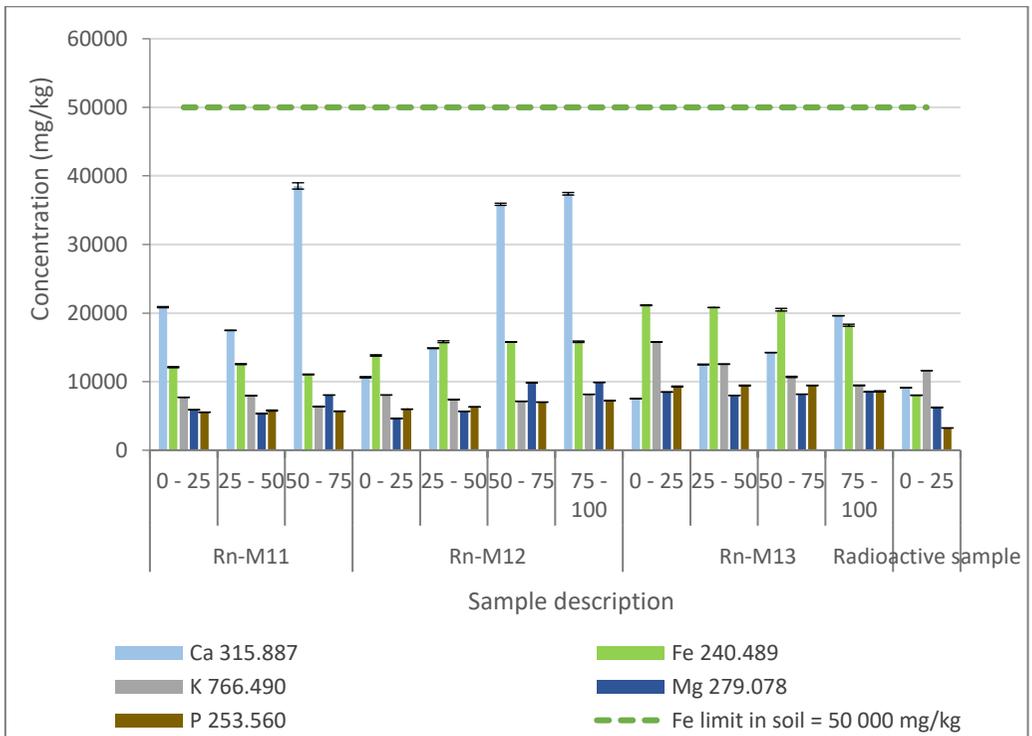


Figure 5. The total concentration of Ca, Fe, K, Mg, and P in soil

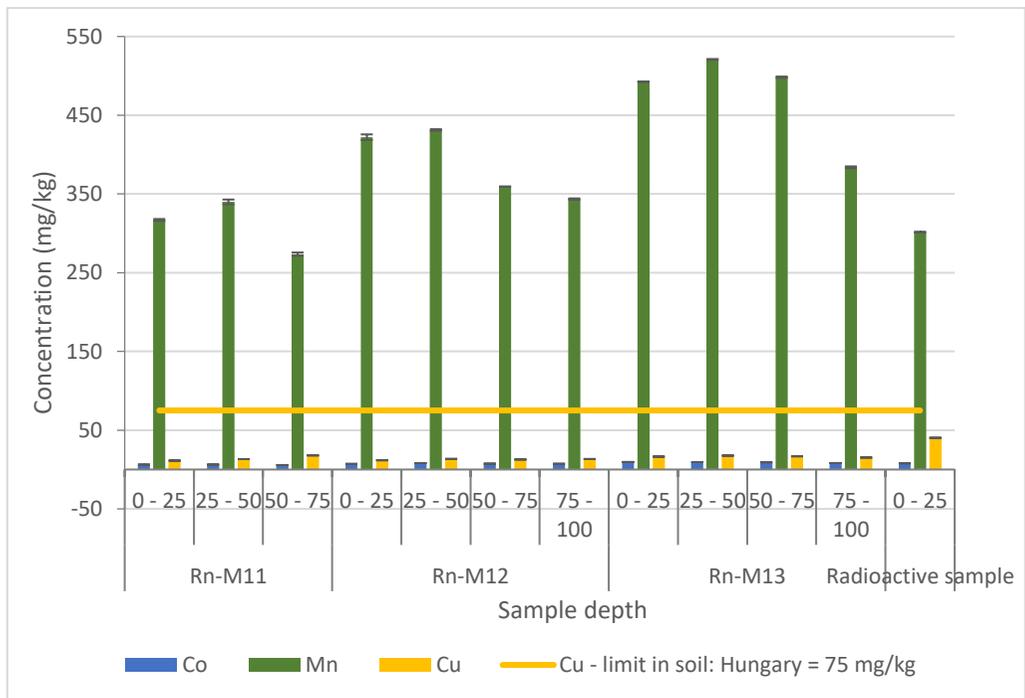


Figure 6. The total concentration of Co, Cu, and Mn, in soil

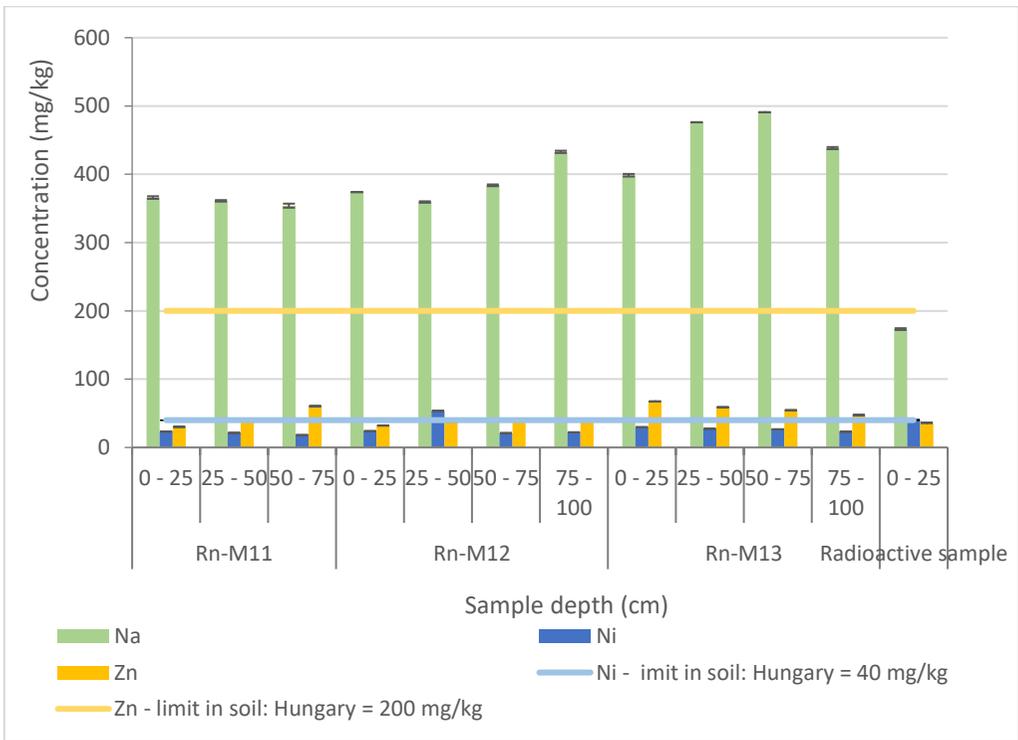


Figure 7. The total concentration of Na, Ni, and Zn in soil

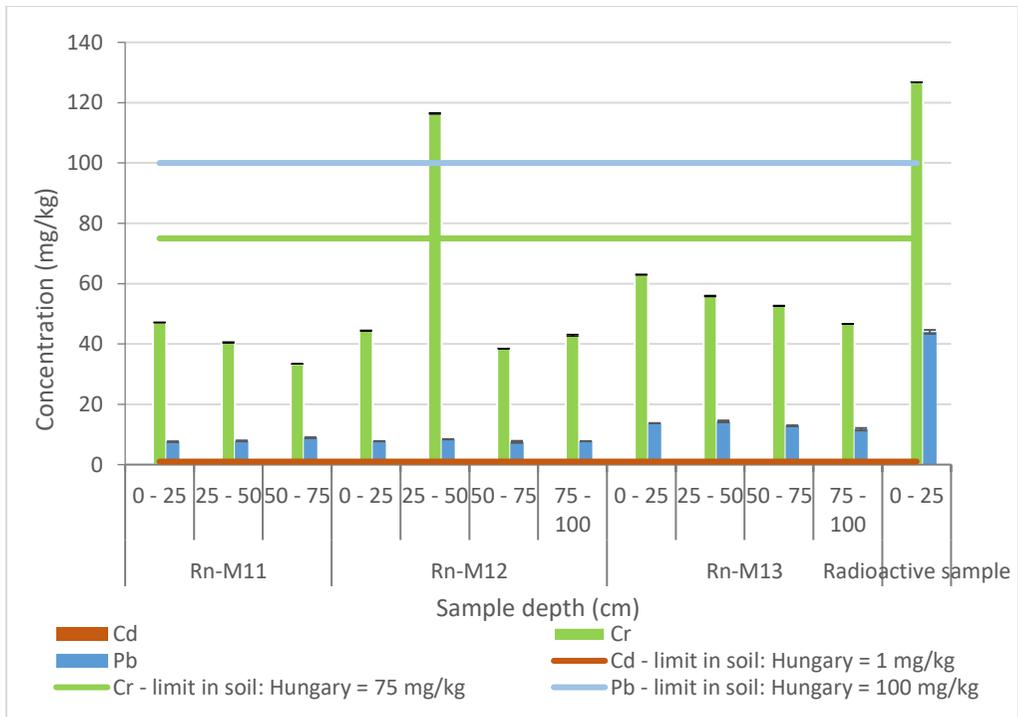


Figure 8. The total concentration of Cr, Cd, and Pb in soil

The average concentrations for PTEs were all within the Hungarian limits for soils collected in Rn-M11, Rn-M12, and Rn-M13. Except for Ni and Cr concentration levels in the Rn-M12 sample at 25 – 50 cm and Radioactive sample were above the limits recommended for soil in Hungary (6/2009. IV. 14. 2009; Rékási and Filep, 2012). However, these Ni and Cr concentrations were still within the allowed values recommended by the Commission of the European Communities (1986).

Most PTE concentrations in soil samples collected from the spoil deposit No. I were lower than the contamination limit values for Hungarian soils and within the permissible limits. The micronutrient results indicated a trend in the increase of concentrations of elements as the slope of the deposit decreased. Soil samples collected from the top of the deposit (Rn-M11) contained less average concentration and the sample collected from the bottom of the deposit (Rn-M13) had the highest average concentration. The Radioactive sample exhibited an abundance of Cr, Cu, Ni, and Pb which could mean that these elements are correlated to U-238. The t-test statistical analysis indicated that there were significant differences in terms of topography with regards to Ca, K, Zn, Cr, and Zn. This observation suggests that as the slope changes, the concentrations of these elements will significantly change. In this case, it is apparent that the water movement down the slope moves some elements in the water direction.

The concentrations for the elements in analyzed plants were compared to the WHO (1996) permissible limits for plants as indicated in (Table 5.).

Table 5. Total concentrations for elements in plant samples

Element	Detection limits	Rn-M11 Concentration (mg/kg)	Rn-M12 Concentration (mg/kg)	Rn-M13 Concentration (mg/kg)	Radioactive unwashed plant Concentration (mg/kg)	Radioactive washed plant Concentration (mg/kg)
Ca	1.30E-05	5710 ± 31.3	4400 ± 9.01	2133 ± 6.89	5369 ± 0.25	5184 ± 24.9

Cd	3.45E-05	n.d.	n.d.	n.d.	n.d.	n.d.
Co	5.64E-05	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	5.59E-05	14.2 ± 0.01	n.d.	n.d.	n.d.	n.d.
Cu	3.35E-05	5.89 ± 0.05	18.3 ± 1.21E-03	59.5 ± 0.07	21.7 ± 0.13	73.1 ± 0.10
Fe	3.81E-05	265 ± 2.08	94.93 ± 0.32	301 ± 1.16	52.39 ± 0.21	68.59 ± 0.20
K	1.12E-03	7206 ± 11.9	7608 ± 87.7	8861 ± 16.0	13289 ± 7.37	14302 ± 3.17
Mg	1.15E-05	1781 ± 7.97	1786 ± 5.06	785 ± 0.51	868 ± 4.30	925 ± 1.69
Mn	8.22E-06	34.2 ± 0.07	21.5 ± 0.11	26.1 ± 0.29	3.68 ± 0.02	8.97 ± 0.06
Na	7.22E-04	73.9 ± 0.31	43.0 ± 0.12	36.9 ± 0.25	33.5 ± 0.87	52.8 ± 0.29
Ni	6.74E-05	5.48 ± 0.03	2.42 ± 0.01	n.d.	n.d.	n.d.
P	4.12E-03	1411 ± 0.28	1150 ± 2.08	1307 ± 0.34	1489 ± 9.02	1631 ± 3.95
Pb	2.21E-04	n.d.	n.d.	n.d.	n.d.	n.d.
U	9.42E-04	13.6 ± 2.33	15.6 ± 2.38	13.7 ± 1.30	11.9 ± 2.05	11.5 ± 1.67
Zn	4.20E-05	20.9 ± 0.03	9.41 ± 0.03	13.6 ± 0.05	8.87 ± 0.02	13.3 ± 0.22

***Permissible values in the plant (mg/kg)**

Cd – 0.8	Cr – 1.3	Cu – 10	Ni – 10	Pb – 2	Zn – 0.6
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Results highlighted in **bold** were above the WHO permissible limits and n.d. refers to not detectable.

*The permissible values in plants (WHO, 1996; Ogundele *et al.*, 2015).

The concentrations of elements in plants were below the WHO permissible values except for Cr in the Rn-M11 sample, Cu in Rn-M12, Rn-M13, and Radioactive (both unwashed and washed plant) samples, and Zn in all the plant samples collected. It could be notable that the plant moisture and average concentrations for plants were having the same trends. There was a minor difference in concentration when comparing the washed and unwashed Radioactive plant samples. This observation indicated that the concentrations of the elements obtained in plants are not due to surface contamination but are due to biological uptake.

The transfer factor (TF) ratios were calculated from the plant shoots and 0 – 25 cm soil depth to determine the ability of a metal species to migrate from the soil into plant roots. The results indicated that the TFs of Cu in Rn-M12 and Rn-M13 samples and K in the Radioactive sample were above the limit of 1. The TF values for Cu indicated an increasing trend from the Rn-M11 with reported TF = 0.52 ± 1.50 , Rn-M12 with TF = 1.56 ± 0.02 , and Rn-M13 with TF = 3.64 ± 14.33 . The

increasing trend implies a Cu migration from the top of the deposit to the bottom of the deposit. According to Fite and Leta (2015), if the TF ratios > 1 , the plants have accumulated elements, the TF ratios approximately one indicate that the elements do not influence the plants, and if the TF ratios < 1 , it is the indication that plants avoid the elements from the uptake.

3.3.2. Uranium concentrations in water

The concentrations of U in water were determined to evaluate the mobility of U from the surrounding spoil deposits into the groundwater and to determine the risks associated with its chemical effects. The U concentrations were measured on the groundwater effluent water and seepage water from the Mecsek uranium mine, and the results were recorded in (Table 6.). The IAEA (2004) reported on the treatment of liquid effluents from uranium mines and mills during and after the operation. In this report, the concentrations for U in process water, pond water, seepage from the dams, and shallow groundwater measured in the Mecsek mine between 1996 and 2000 were reported and are listed in (Table 6.) below. In Hungary, the research of natural radioactivity of groundwater is an important issue since both the drinking water supply and the bottled mineral water market rely almost 100 % on groundwater (Eróss *et al.*, 2018). Therefore, the groundwater concentrations obtained in this study were compared to the total uranium guideline value of 0.03 mg/L in drinking water set by WHO (2004). In contrast, the effluent water and the seepage water results were compared to the U_{\max} limit of 2 mg/L regulated by the Hungarian Ministerial Decree. All the water results obtained in this study were also compared to the results that were previously obtained in the Mecsek uranium mine and published by the IAEA (2004).

Table 6. Uranium concentrations for water samples

Results from the current study	Results from the IAEA (2004) Study
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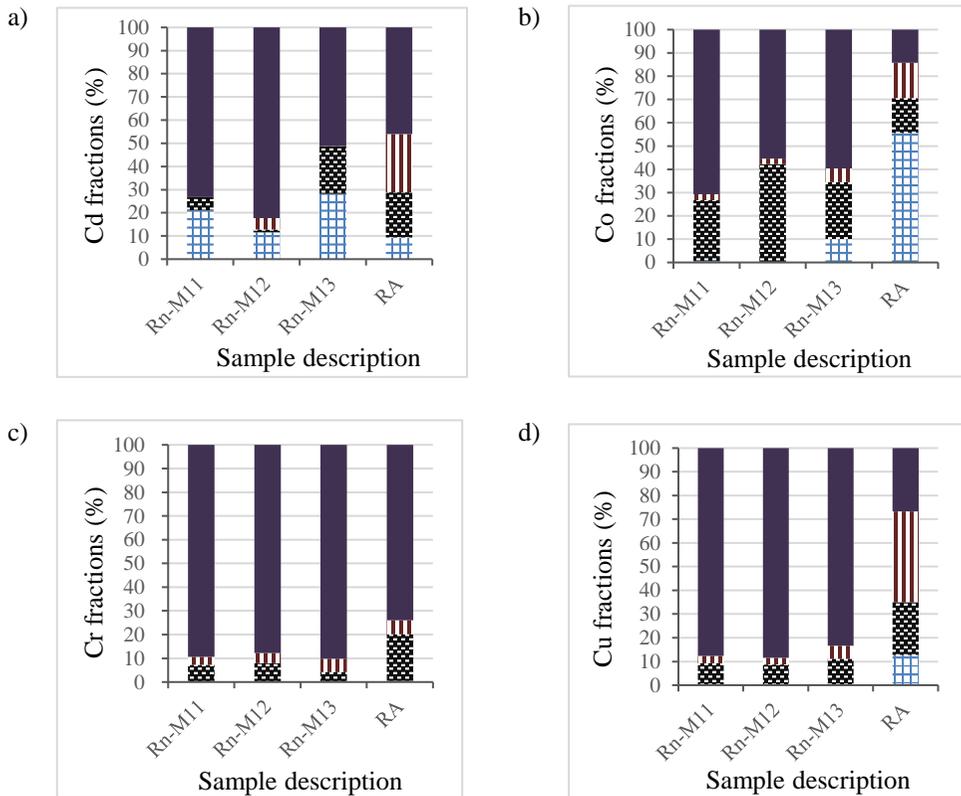
Sample ID	Sample description	U concentration (mg/L)	Sample description	U concentration (mg/L)
PK-33/1	Groundwater (No. I)	6.06 ± 0.03	groundwater	0.01 – 0.04
PK-44/3	Groundwater (No. I)	0.23 ± 0.001	pond water	0.03
PK-29/1	Groundwater (No. I)	1.87 ± 0.01	process water	< 0.5
1504/1	Groundwater (No. I)	2.78 ± 0.01	seepage water	2 - 5
P-2/5	Groundwater (No. II)	1.90 ± 0.06		
P-2/6	Groundwater (No. II)	0.52 ± 0.003		
Elfolyó	treated mine water	0.32 ± 0.001		
6/11 Szint	mine water from the spoil deposit No. I	2.46 ± 0.01		
Északi-tározó	mixed water: mine water from the waste deposit No. III and leaking water from precipitation	6.72 ± 0.04		
IIIM. Gyűjtő	seepage water from the waste deposit No. III	6.99 ± 0.02		
Cs-0	seepage water from the waste rock pile No. II	0.84 ± 0.003		

Groundwater sample PK-33/1 collected near the spoil deposit No. I indicated an elevated U concentration of 6.06 ± 0.03 mg/L which is above the WHO guideline value for U (0.03 mg/L) in drinking water (WHO, 2004). All groundwater samples collected in this study were above the WHO guideline value. The comparison of U concentration in this study and the study conducted by IAEA (2004) indicated that U concentrations in groundwater for this study ranged from 0.23 ± 0.001 mg/L to 6.06 ± 0.03 mg/L. In contrast, the U concentrations from the IAEA study ranged from 0.01 mg/L to 0.04 mg/L. Overall, the U

concentrations in mine water for this study ranged from 0.32 ± 0.001 mg/L to 6.72 ± 0.04 mg/L, whereas the U concentrations from the IAEA study were < 0.5 mg/L.

3.3.3. The mobility of PTEs and uranium by BCR sequential extraction

The concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, U, and Zn in fractions F1, F2, F3, and F4 were determined for the 0 – 25 cm soil depth. The average percentage distribution of PTE concentrations for each sample (where RA represents Radioactive sample) in different fractions of the modified BCR is presented in (Figure 8.) and in (Table 7.).



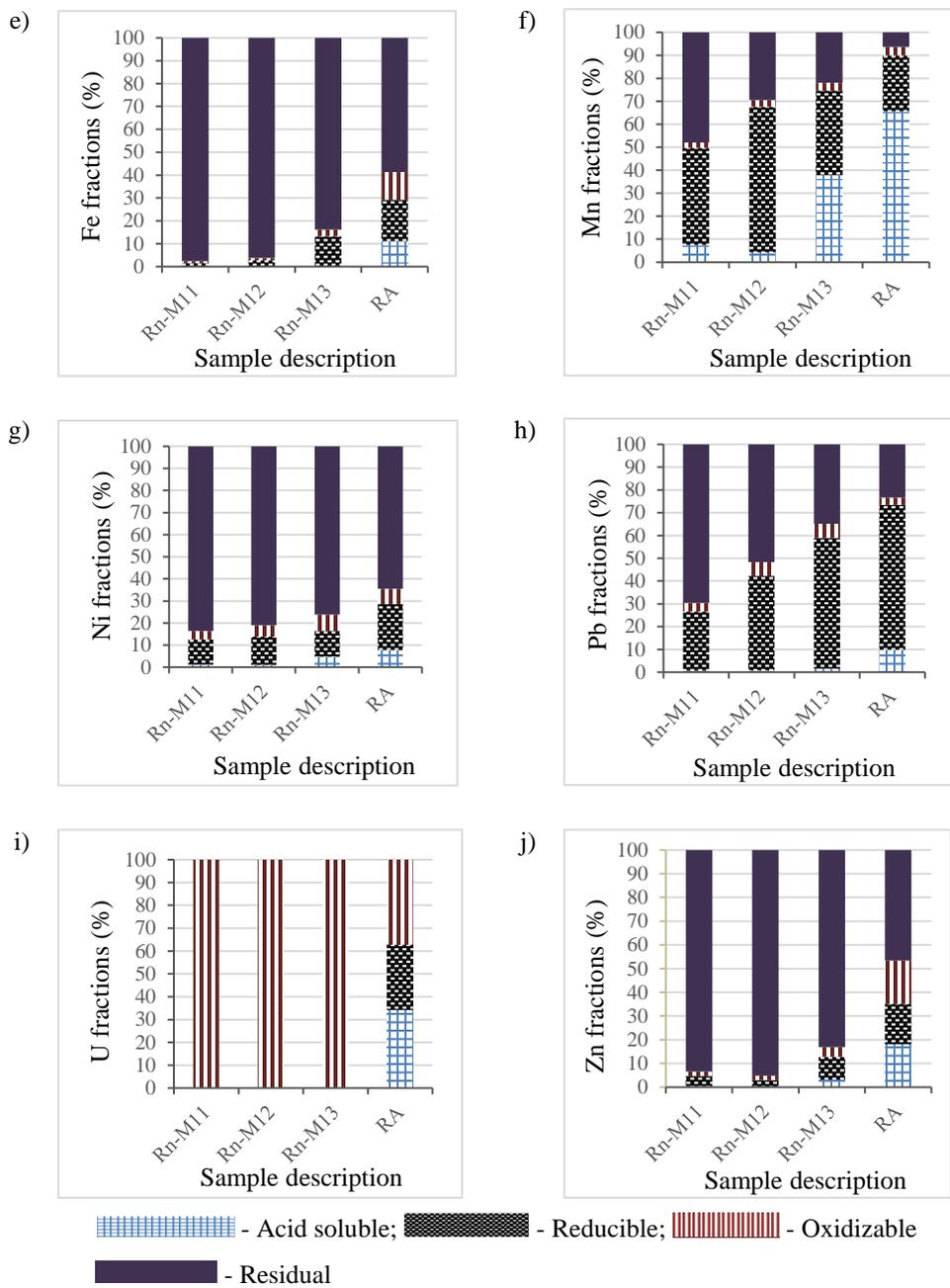


Figure 9. The average percentage for the distribution of extractable content (average %) of a) Cd, b) Co, c) Cr, d) Cu, e) Fe, f) Mn, g) Ni, h) Pb, i) U, and j) Zn in soil from uranium mine spoil bank

Table 71. Average concentrations for each fraction of the BCR sequential extraction and pseudo total concentrations with standard uncertainties

Fraction 1 – Acid soluble					
Element	Instrumental detection limit (mg/kg)	Concentration ± standard uncertainty (mg/kg)			
		Rn-M11	Rn-M12	Rn-M13	Radioactive sample
Cd	3.45E-05	0.03 ± 4.83E-03	0.01 ± 0.01	0.05 ± 0.01	0.06 ± 0.02
Co	5.64E-05	0.05 ± 0.02	0.02 ± 0.01	0.81 ± 0.03	4.27 ± 1.84
Cr	5.59E-05	0.07 ± 0.01	0.10 ± 0.02	0.07 ± 0.01	0.30 ± 0.11
Cu	3.35E-05	n.d.	n.d.	0.08 ± 0.02	5.08 ± 2.21
Fe	3.81E-05	0.57 ± 0.53	0.30 ± 0.23	7.02 ± 0.57	824 ± 366
Mn	8.22E-06	31.1 ± 0.17	19.5 ± 1.37	166 ± 2.94	202 ± 88.1
Ni	6.74E-05	0.43 ± 0.21	0.32 ± 0.05	1.20 ± 0.02	2.28 ± 0.97
Pb	2.21E-04	0.10 ± 0.06	0.08 ± 0.20	0.20 ± 0.18	4.34 ± 2.16
U	9.42E-04	n.d	n.d	n.d	17.4 ± 7.46
Zn	4.20E-05	0.19 ± 0.25	n.d	2.05 ± 0.42	5.84 ± 2.15
Fraction 2 - Reducible					
Element	Instrumental detection limit (mg/kg)	Rn-M11	Rn-M12	Rn-M13	Radioactive sample
Cd	3.45E-05	0.01 ± 3.96E-03	n.d	0.04 ± 2.62E-03	0.12 ± 0.05
Co	5.64E-05	2.23 ± 0.08	3.33 ± 0.11	1.99 ± 0.04	1.14 ± 0.53
Cr	5.59E-05	6.00 ± 0.23	5.09 ± 1.37	2.10 ± 0.74	16.6 ± 9.41
Cu	3.35E-05	1.47 ± 0.02	1.35 ± 0.03	2.07 ± 0.22	8.89 ± 3.54
Fe	3.81E-05	4547 ± 17.9	584 ± 22.5	2805 ± 99.7	1349 ± 567
Mn	8.22E-06	177 ± 4.81	286 ± 11.0	161 ± 4.75	75.0 ± 39.0
Ni	6.74E-05	4.42 ± 0.22	4.09 ± 0.53	3.01 ± 0.37	6.14 ± 3.89
Pb	2.21E-04	3.35 ± 0.04	3.92 ± 0.07	7.18 ± 0.11	28.2 ± 11.7
U	9.42E-04	n.d	n.d	n.d	14.5 ± 5.77
Zn	4.20E-05	2.38 ± 0.36	1.32 ± 0.31	6.32 ± 0.29	5.50 ± 2.46
Fraction 3 - Oxidizable					
Element	Instrumental detection limit (mg/kg)	Rn-M11	Rn-M12	Rn-M13	Radioactive sample
Cd	3.45E-05	n.d	0.01 ± 2.60E-03	n.d	0.16 ± 0.07
Co	5.64E-05	0.22 ± 0.02	0.19 ± 0.02	0.48 ± 0.02	1.17 ± 0.51
Cr	5.59E-05	2.76 ± 0.09	2.87 ± 0.42	2.99 ± 0.50	4.84 ± 2.17
Cu	3.35E-05	0.50 ± 0.11	0.44 ± 0.10	1.05 ± 0.05	15.2 ± 6.98
Fe	3.81E-05	213 ± 4.09	192 ± 5.04	586 ± 27.8	898 ± 376
Mn	8.22E-06	9.78 ± 0.27	13.0 ± 0.32	14.8 ± 0.62	11.3 ± 5.11
Ni	6.74E-05	1.49 ± 0.03	1.64 ± 0.10	1.90 ± 0.10	2.05 ± 0.81
Pb	2.21E-04	0.48 ± 0.33	0.57 ± 0.25	0.77 ± 0.50	1.41 ± 1.00
U	9.42E-04	1.28 ± 0.21	2.07 ± 0.15	3.19 ± 0.12	18.9 ± 7.50
Zn	4.20E-05	1.04 ± 0.14	0.85 ± 0.21	2.72 ± 0.09	5.91 ± 2.28
Fraction 4 – Residual					

Element	Instrumental detection limit (mg/kg)	Rn-M11	Rn-M12	Rn-M13	Radioactive sample
Cd	3.45E-05	0.11 ± 0.03	0.09 ± 0.01	0.10 ± 0.02	0.29 ± 0.03
Co	5.64E-05	6.03 ± 0.30	4.39 ± 0.55	4.84 ± 0.28	1.09 ± 0.13
Cr	5.59E-05	74.5 ± 2.63	57.6 ± 4.58	47.3 ± 7.51	62.1 ± 6.80
Cu	3.35E-05	13.9 ± 0.28	13.7 ± 0.74	16.1 ± 0.90	10.7 ± 2.42
Fe	3.81E-05	26731 ± 4018	19861 ± 3.11	17681 ± 1639	4360 ± 430
Mn	8.22E-06	201 ± 24.4	133 ± 22.8	96.6 ± 5.00	19.7 ± 3.28
Ni	6.74E-05	32.3 ± 1.31	25.9 ± 0.97	19.5 ± 3.16	19.0 ± 3.30
Pb	2.21E-04	8.98 ± 3.22	4.87 ± 1.37	4.36 ± 0.45	10.4 ± 2.22
U	9.42E-04	n.d	n.d	n.d	n.d
Zn	4.20E-05	50.9 ± 1.76	42.5 ± 5.82	54.5 ± 2.98	15.1 ± 2.05

The n.d. abbreviation refers to not detectable

The quality control for the BCR sequential procedure was conducted using the Certified Reference Material (CRM) BCR[®]-701, and the results were all above 76.4 %. The results produced acceptable recoveries except for Pb in the acid-soluble fraction, which indicated a very low yield of 1.95. In addition, the validation of the BCR sequential procedure was conducted. It indicated a slight difference between the sum of the concentrations cumulated concentrations of fractions (F1+F2+F3+F4) in the BCR procedure and the pseudo total concentrations.

The BCR sequential extraction results indicated that the percentages of the extractable amount of U, Mn, Pb, Co, and Cd in the non-residual fractions were subsequently high (ranging from 36.8 % to 100 %). High percentages of these PTEs in mobile fractions might lead to the high bioavailability of these elements, leading to toxicity if not properly handled (Zimmerman and Weindorf, 2010; Okoro *et al.*, 2017). The average percentage of Cd (17.5 %) in the acid-soluble fraction presents a significant environmental hazard, considering the high toxicity of Cd (Ma *et al.*, 2011). Although the percentage in the acid-soluble fraction is minimal, this fraction is more mobile and dangerous relative to other fractions, and thus, the pollution may become substantially high (Soltani *et al.*, 2017).

The results obtained imply that the Radioactive sample had the highest quantity of PTEs bound to the non-residual fractions. The topographic conditions and the anthropogenic activities may have contributed to the amount of concentration found in these sample locations and the amount being released into the environment. The Radioactive sample, which was sampled from the bottom of the spoil deposit, had lower pH, lower CEC with a higher PTE distribution percentage, whereas the samples collected from the top of the deposit and on the slope showed slightly higher pH, higher CEC, with less PTE distribution percentage. This could be due to the leaching from the spoil rock and transportation along by the lateral water stream horizontally from the top of the deposit to the bottom of the deposit. Additionally, there was no trend in depths; the PTE concentrations varied throughout different depths of each sample.

The mobility of PTEs in soil

The fractions weakly bound to soil components (acid-soluble, reducible, and oxidizable) were used to assess the mobility of elements in soil (Kabala and Singh, 2001). The mobility factor was calculated, and the results indicated the mobility of PTEs was in the following order:

- ❖ Rn-M11 sample: $U > Mn > Pb > Co > Cd > Ni > Cu > Cr > Zn > Fe$,
- ❖ Rn-M12 sample: $U > Mn > Pb > Co > Ni > Cd > Cr > Cu > Zn > Fe$,
- ❖ Rn-M13 sample: $U > Mn > Pb > Cd > Co > Ni > Zn > Cu > Fe > Cr$, and
- ❖ Radioactive sample: $U > Mn > Co > Pb > Cu > Cd > Zn > Fe > Ni > Cr$.

The mobility order for all the samples asserts that U followed by Mn and Pb were highly mobile in this study, while Fe, Zn, and Cr were less mobile. This data reveals that Cd, Mn, Pb, and U were more available for mobility than other PTEs in this study.

3.3.4. Statistical analysis

The BCR procedure

The statistical analysis for the BCR procedure indicated that a strong significant correlation existed between the pH, CEC, Co, Ni, and Fe. When the pH and CEC decreased, these elements were increasing in the non-residual fractions. In this statistical analysis, there was a significant relationship among Cd, Cr, Pb, U, and Cu at $p \leq 0.05$. The results implied that where U is mobile, there is a high possibility that Cd, Cu, and Pb will also be available. One-sample t-test analysis indicated that the concentrations for each PTE obtained using a BCR sequential extraction procedure were significantly different in each fraction for Cd, Cr, Co, Cu, U, Pb, Mn, and Fe.

Linear regression analysis was performed to determine the soil's effect on the plants using the soil concentrations from the sum of the mobilized fractions (obtained using a BCR method) and the plant concentrations. The results were statistically insignificant for most of the elements. The results indicated that the correlations between the soil and the plants for each element were not strong except for U, which showed $R = 0.794$, $p > 0.05$. In fact, all the p values in this analysis were above the 0.05 significance level. The unstandardized coefficient B resulted in negative values except for Fe, which showed a positive but low value. In summary, these observations suggest that the mobilized element from the BCR method are not being taken up by the plants. In this case, the BCR method could not be considered to determine the elemental plant uptake from the soil.

The soil characteristics

The observations for the soil characteristics, pseudo total, and radionuclides indicated a weak positive correlation between the pairs pH – % SM and CEC – pH; however, the pair CEC – % SM showed a weak negative correlation. The results indicated a strong correlation between the % SOM and the % SM ($r = 0.75$; $p \leq 0.05$). Additionally, % SOM had a strong correlation ($p \leq 0.05$) with Zn ($r = 0.86$), K-40 ($r = 0.78$), and K ($r = 0.78$). However, the % SOM was observed to have a weak relationship with the radionuclides, the pH, and the CEC. The One-

Sample t-test showed that the SOM values were significantly different in all three depths considered for this analysis when considering the topography. In contrast, the CEC was only significantly different in 25 – 50 cm depth. In terms of depth, CEC and SOM were found to be significantly different in Rn-M11

The pseudo total procedure

The correlation matrix between radionuclides and pseudo total PTEs indicated a significant relationship ($p \leq 0.05$) between (U-238: U-235, Rn-222, and Cu); (Th-232: Fe, P, Na, and Mn); and (K-40: K, Co, Mn, Zn, Fe, and P). The observations among PTEs resulted in the strong significant correlation matrices ($r > 0.60$; $p \leq 0.05$) among Fe, P, Co, Mn, Na, and Zn. Cobalt and Mn were common in these correlation matrices.

The principal component analysis (PCA) correlation biplot indicated that most of the elements contribute to the positive side of the principal component two (PC 1) and the negative side of the PC 2. The radioactive elements (U-238, U-235, and Rn-222) indicated a strong correlation with the PTEs (U, Ni, Pb, Cu, and Cr). It could be observed that the CEC and the pH were diagonally opposite the U-238, U-235, and Rn-222, including all the PTEs that are correlated with these elements.

One-Sample t-test statistical analysis results indicated that the total concentrations of PTEs and radionuclides were statistically significant ($p \leq 0.05$) for the depths of Rn-M12 and Rn-M13 samples; in contrast, for the Rn-M11 sample, indicated the significant differences in depths for U-238, U-235, Rn-222, and Ca. The statistical analysis considering the topography (Rn-M11, Rn-M12, and Rn-M13) indicated that there were no significant differences among the sampling locations. However, when the Radioactive sample was included in the statistical analysis, there were significant differences among the concentrations of U-238, U-235, Rn-222, and Ca in different locations.

4. CONCLUSION AND RECOMMENDATIONS

The activity concentrations of K-40, U-238, and Th-232 radionuclides indicated high activity concentrations in all soil and plant samples collected from the Mecsek uranium mine at Pecs. The concentrations for these three natural radionuclides were above the Hungarian mean values and the World's median values as specified by UNSCEAR (2000). The vertical distribution of activity concentrations for all the natural radionuclides in all depth levels did not follow any trend; the results varied throughout for all sample locations. However, It could be noted that the samples collected from the bottom of the deposit (Rn-M13 and Radioactive samples) had elevated activity concentrations as compared to the samples collected from the top and on the slope of the deposit. This increase in concentrations is due to the leaching from the spoil matter through the cover soil layer along the slope of the deposit.

Most PTE concentrations in soil cover samples collected from deposit No. I were lower than the contamination limit values for Hungarian soils and within the permissible limits. The results for some elements indicated a trend in the increase of concentrations of elements as the slope of the deposit decreased.

The results for PTEs in plants indicated that there was a possibility that these elements were available for uptake by the plants. Similarly, radionuclides activity concentrations were observed to be elevated in plants for all the samples collected from spoil deposit No. I. The unnoticeable difference in the results for the washed and unwashed radioactive samples eliminated the possibility that the concentrations detected in plant samples might be due to the surface contamination caused by the wind erosion. The transfer factor values calculated from the pseudo total concentrations indicated a likelihood of radionuclide and PTE uptake by plants. The linear regression analysis for the determination of soil's effect on plants using the sum of the BCR mobile fractions indicated that there is

no evidence that the plants have taken up the elements from these mobile fractions. This could be due to the plants having different plant genotypes, and agronomic management, and different type of plant root systems, and the response of plants to elements. In this case, the BCR method could not be used successfully to predict the possibility of plant uptake. However, the transfer factor calculations using pseudo total could be successfully applied for the prediction of plant uptake.

It was observed that all groundwater samples collected in this study were above the WHO guideline value. Elevated U concentrations in groundwater are of concern because it indicates active processes of the uranium leaching from the spoil deposits. It also shows the capability of elements migrating into the groundwater. The elevated U levels in groundwater may be due to the seeping of water containing high concentrations of U from the process water. These findings explained the need for Mecsekérc Zrt. (2017) to focus more on waste rock dumps No. I to ensure that the remediation process is successful. Based on the high levels of U in groundwater, it could be concluded that the soil cover layer requires an additional step to ensure that its integrity is intact.

The possibility of migration of PTEs was confirmed using fractionation by sequential extraction for PTEs. The high average percentage of U, Mn, and Pb and a high percentage of U, Mn, Pb, and Cd in non-residual fractions indicates that there is a possibility being released may become a threat to the environment by subsequently becoming available to be taken up by plants (Pavlović *et al.*, 2018; Pérez-Moreno *et al.*, 2018). Although these elements exhibit high percentages in non-residual fractions, a large part of these percentages come from the Radioactive sample, which is radioactive and highly contaminated with U. Therefore, the location where Radioactive sample was taken from should be considered as a potential hazard to the environment. The fractional distribution of the Radioactive sample shows that the mobility, availability, and vertical transport of metals are surprisingly different (Fedotov *et al.*, 2018). The U, Cd, Co, Mn,

Cu, Pb, and Zn fractional distribution in the Radioactive sample indicates that some parts of the spoil deposit require additional steps to protect the environment.

Based on the statistical analysis, a significant correlation between the pH and the CEC existed; therefore, it was concluded that these soil chemical properties have an impact on each other. Additionally, the pH had a significant relationship with Co, Fe, and Ni; and the CEC had a significant relationship with Co, Fe, and Ni, whereas the relationship between the CEC and Cr was not significant). It was observed that pH and CEC relationship with the radionuclides was not significant. However, soil moisture had a significant relationship with Th-232. When considering the topography, it was observed that the SOM values were significantly different in all three depths that were considered for this analysis, whereas the CEC was only significantly different in 25 – 50 cm depth. In terms of depth, CEC and SOM were found to be significantly different in Rn-M11. There was a strong significant relationship between radionuclides and some PTEs, suggesting their common origin (Bai *et al.*, 2017). The principal component analysis biplot analysis for soil indicated that when the pH, CEC, and Ca are high, the mobility of U, U-235, U-238, Cu, Cr, Pb, Rn-222, and Ni decrease. Furthermore, there was a very strong relationship among Cd, Cr, Pb, U, and Cu, which is significant at a 95 % confidence level. These results imply that where U is mobile, there is a high possibility that Cd, Cu, and Pb will also be available. The main trend of the concentration changes along the slope (considering only Rn-M11, Rn-M12, and Rn-M13), One-Sample t-test indicated that there was an increase of element concentrations from the top to bottom direction. In the case of Rn-222, U, Ca, Ni, Zn, Cr, and Ni, the difference was significant. However, when the Radioactive sample was considered, an increase of U-238, U-235, and Pb was significant. The vertical distribution of PTEs and radionuclides did not show unambiguous trends; it was different for element to element and sampling position on the slope. The results indicated that only the Rn-M11 sample had

elements that were significantly different as the depth deepens. In this sampling location, U-238, U-235, Rn-222, and Ca were significantly different. These results show that two samples (Rn-M11 and Radioactive samples) which did not have sufficient (1 m) soil cover, show significant differences in concentrations for some elements.

Therefore, as stated by Sungur *et al.* (2014), the BCR sequential extraction procedure has proven to be useful in providing information regarding the mobility of PTEs for the planning and management of recultivation applications. The concentrations for each PTE obtained using a BCR sequential extraction procedure were significantly different in each fraction for Cd, Cr, Co, Cu, U, Pb, Mn, and Fe. Based on the plant radionuclidic and PTE uptake; and on the results from the BCR sequential extraction, it is apparent that one meter (1 m) intact of the soil cover layer for spoil deposit No. I is enough for effective retardation of migration of PTEs and radionuclides. However, where the soil cover layer thickness is low (Radioactive sample), it is not compelling enough. Therefore, additional soil cover is needed to stabilize and protect the environment to ensure environmental safety. Additionally, since the sampling of soil sample in 75 – 100 cm depth in Rn-M11 and 25 – 100 cm for Radioactive sample was not possible due to the rocks underneath, it is an indication that the cover layer was not 1 m in these locations as recommended by the OECD/NEA (2014).

As a summary, it can be concluded that the BCR sequential extraction is an appropriate tool for the identification of leakages through the wounded remediation cover soil layer. Despite the relatively low pseudo-total concentration of the PTEs, the sequential extraction proves additional information on their mobility by water infiltration. These results of the BCR sequential extraction confirm the establishment based on the measuring of pseudo total concentration and plant uptake. This methodology has proven to be appropriate for application in similar circumstances in South Africa.

4. NEW SCIENTIFIC RESULTS

1. Radionuclide and PTE concentrations in the soil cover layer of the spoil deposit No. I take their origin from the soil's own matter and from the spoil rock due to the leaching and migration by water infiltration vertically and along the slope. The distribution of PTE and radionuclide concentrations in the soil cover layer depends on the chemical character of an element and soil characteristics (pH, CEC, SOM, Soil moisture, etc.) and has shown different patterns for different elements. The main trend of the concentration changes along the slope (considering only Rn-M11, Rn-M12, and Rn-M13), there was an increase of element concentrations from the top to bottom direction. In the case of Rn-222, U, Ca, Ni, Zn, Cr, and Ni, the difference was significant. However, when the Radioactive sample was considered, an increase of U-238, U-235, and Pb was significant. The soil samples at the bottom of the deposit (Rn-M13) had the highest average SOM, soil moisture, and the least pH values; however, the CEC varied for all samples. The vertical distribution of PTEs and radionuclides did not show unambiguous trends; it was different for element to element and sampling position on the slope. At the wounded sampling location (Radioactive sample), where the soil cover layer was only 25 cm, significantly higher PTE and radionuclide concentrations were measured.
2. The mobility of different elements in the soil cover layer was detected by the BCR fractionation. In the upper (0-25 cm) covering soil layer, the BCR fractionation results have shown that the abundance of U (100%), Mn (73.5 %), Pb (55.1%), and Cd (36.8 %) was present in mobile fractions and this is an indication that these elements may move together along the slope of deposit by water. The mobility of PTEs at all sampling locations (average mobility factor) followed the order: $U > Mn > Pb > Co > Cd > Cu > Ni > Zn > Fe > Cr$. The mobility of U was confirmed by total

concentrations in all four groundwater samples collected near spoil deposit No. I; PK-33/1 (6.06 ± 0.03 mg/L), PK-44/3 (0.23 ± 0.001 mg/L), PK-29/1 (1.87 ± 0.01 mg/L), and 1504/1 (2.78 ± 0.01 mg/L) which were all above the WHO guideline value for U (0.03 mg/L) in drinking water.

3. The concentrations of U-238, Th-232, K-40, Cr, Cu, and Zn in plant samples and the TF transfer factor values for U-238, U-235, Th-232, K-40, Cu, and K indicated that these elements were easily available for uptake from soil to plants. Using the pseudo total soil concentrations for TF calculation, problem areas could be identified, and applying the BCR sequential extraction method helped to specify the elements prone to mobility and bioavailability according to environmental conditions in the Mecsek uranium mine.
4. The combination of the BCR sequential extraction and pseudo total methodologies used in this study discovered some problems regarding the efficacy of the recultivation soil in uranium mine areas; thus, it is possible to make additional proposals for more supplementary remediation processes which are necessary. It was proved that the soil cover layer satisfactory retard the migration of the PTEs and radionuclides from the spoil leaching. However, when it is wounded, it may cause the release of these contaminants into the groundwater and surrounding environment. The BCR sequential extraction has proven to identify mobile elements in uranium mine deposits. Therefore, this methodology should be an appropriate tool in evaluating environmental contamination. As a result, this fractionation method should be included in the monitoring program.

5. PUBLICATIONS RELATED TO THE DISSERTATION

1. Publication (Journal Article: Q2 - IF = 3.5)

Heltai, György; Györi, Zoltán; Fekete, Ilona; Halász, Gábor; Kovács, Katalin; Takács, Anita; Khumalo, Lamlile; Horváth, Márk. Application of flexible multi-elemental ICP-OES detection in fractionation of potentially toxic element content of solid environmental samples by a sequential extraction procedure. MICROCHEMICAL JOURNAL 149 Paper: 104029, 7 p. (2019). DOI WoS REAL Scopus.

2. Publication (Journal Article: Q3 - Peer-reviewed)

Lamlile, Khumalo; György, Heltai; Mark, Horvath. The migration of potentially toxic elements during the recultivation of the uranium mining deposit in Mecsek. ACTA HYDROLOGICA SLOVACA 20: 2 pp. 210-217, 8 p. (2019). DOI Egyéb URL. Publication:30974882.

3. Publication (Journal Article: Q3 – IF = 1.5) – Accepted on the 11th June 2021

Lamlile Khumalo, György Heltai, András Várhegyi and Márk Horváth. Evaluating the mobility of potentially toxic elements from the uranium mine spoil bank using the BCR sequential extraction procedure. ECOLOGICAL CHEMISTRY AND ENGINEERING S (ECE S).

4. Oral presentation (Conference paper)

Lamlile, Khumalo; Mark, Horvath; György, Heltai, Characterization of mobility of potentially toxic elements in soil-water system by sequential extraction procedures In: Jakab, G Tóth A Csengeri E (eds.) Alkalmazkodó vízgazdálkodás: lehetőségek és kockázatok Szarvas, Hungary: Szent István Egyetem Agrár- és Gazdaságtudományi Kar, (2018) pp. 260-266., 7 p.

22 March 2018, Szarvas, Hungary.

5. Oral presentation (Abstract)

Khumalo, Lamlile; Heltai, György; Horváth, Márk, Evaluation of the ecological risk caused by the mobility of radioactive elements and potentially toxic

elements during the recultivation of the uranium mining deposit No.1 in Mecsek, 18th Alps-Adria Scientific Workshop. 1– 6 April 2019, Cattolica, Italy.

6. Oral presentation (Abstract)

Lamlile, Khumalo; Mark, Horvath; Gyorgy, Heltai, Sampling procedure for monitoring processes for the mobility of radioactive elements and potentially toxic elements during the recultivation of the uranium mining deposit No.1 in Mecsek, XXI. Századi vízgazdálkodás a tudományok metszéspontjában: II. Víz tudományi Nemzetközi - Konferencia. 22 March 2019, Szarvas, Hungary.

7. Poster (Abstract)

Lamlile, Khumalo; György, Heltai; Miklós, Czémán; András, Várhegyi; Gábor, Németh; Gábor, Földing; Csaba, Alföldi; Mark, Horvath, Evaluation of the ecological risk caused by the mobility of radioactive and potentially toxic elements during the recultivation of the uranium mining deposit No. 1 in Mecsek, XVI Hungarian - Italian Symposium on Spectrochemistry: technological innovation for water science and sustainable aquatic biodiversity & 61st Hungarian Spectrochemical Conference. 2– 6 October 2018, Budapest, Hungary.

8. Oral presentation (Abstract)

György Heltai; Zoltán Győri; Ilona Fekete; Gábor Halász; Katalin Kovács; Anita Takács; Lamlile Khumalo; Márk Horváth. Fractionation of potentially toxic elements in sediment/soil/water system by a sequential extraction procedure applying flexible multielemental spectrochemical detection in remediation of contaminated areas. In: Mihucz, Viktor Gábor (eds.) XVI Hungarian - Italian Symposium on Spectrochemistry: technological innovation for water science and sustainable aquatic biodiversity & 61th Hungarian Spectrochemical Conference: October 3-6, 2018, Budapest: programme & book of abstracts. Budapest, Hungary: MKE (2018) 118 p. p. 49
Paper: KL04

9. Oral presentation (Abstract)

Khumalo, L.H.N.; Heltai, Gy.; Horvath, M. Mobility of radionuclides from the spoil deposit No.1 of the abandoned uranium mine in Pécs, Hungary In: 5th International Conference on Environmental Radioactivity (ENVIRA2019): Variations of Environmental Radionuclides. (2019) p. 67 Paper: ID 89. 8 – 13 September 2019, Prague, Czech Republic.

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